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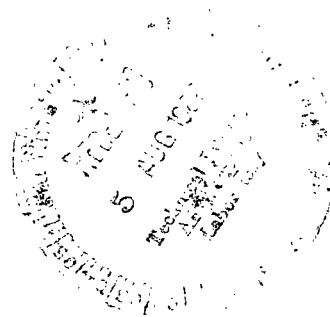


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CHROMIUM AND NICKEL POWDERS MADE BY REDUCTION OF THEIR OXIDES WITH MAGNESIUM, LITHIUM, OR SODIUM VAPORS

by Alan Arias

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Cleveland, Ohio*



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ABSTRACT

Chromium powder separable into 0.0068- μm colloidal and 0.16- μm coarse powder fractions was obtained by reduction of Cr_2O_3 with Mg vapor in a vacuum furnace. The coarse powder fraction was calculated to have 8 volume percent residual MgO plus $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ dispersoids, probably suitable for dispersion strengthening. Other chromium powders, 0.08- to 0.60- μm particle size and oxygen to surface area ratios of about 0.002 g/m^2 , were made by reduction of Cr_2O_3 with Li and Na vapors. Nickel powder, 1.25- μm particle size and with 0.114 percent oxygen, was made by reduction of NiO with Li vapor.

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SUMMARY

This exploratory investigation was conducted to determine the feasibility of producing relatively pure, ultrafine particle size chromium and nickel powders, suitable for dispersion strengthening, by reduction of the corresponding metal oxides with vapors of reactive metals.

On reducing chromic oxide (Cr_2O_3) with magnesium vapor at 770°C , a chromium powder was produced which was separated into a colloidal (5 weight percent) and a coarse (95 weight percent) fraction. The colloidal and coarse fractions yielded 0.0068- and 0.16- micrometer powders and had 2.24 and 1.74 weight percent oxygen, respectively. The coarse chromium fraction had 1.16 weight percent residual magnesium. Calculations showed that this magnesium could form 7.68 volume percent magnesium oxide (MgO) plus magnesium oxide - chromic oxide ($\text{MgO} \cdot \text{Cr}_2\text{O}_3$) spinel. A compact prepared from such a powder should exhibit dispersion strengthening and perhaps a low ductile-to-brittle transition temperature.

On reducing Cr_2O_3 with lithium vapor at temperatures from 420° to 800°C , powders with particle sizes from 0.078 to 0.589 micrometer and oxygen contents from 1.50 to 0.176 weight percent, respectively, were obtained.

Reduction of Cr_2O_3 with sodium vapor at 510°C yielded 0.015-micrometer chromium powder with 7.14 weight percent oxygen. At higher temperatures, the reaction was impeded by an impervious chromic oxide - sodium oxide ($\text{Cr}_2\text{O}_3\text{-Na}_2\text{O}$) layer.

Reduction of nickel monoxide (NiO) with lithium vapor at 600°C yielded 1.25-micrometer nickel powder with 0.114 weight percent oxygen. This powder compares favorably in particle size and purity with commercially available nickel powders.

It is surmised that reduction of pulverized oxide melts with lithium vapor could be used for producing nickel-chromium (perhaps with dispersoids) alloy powders.

Despite the wide range in surface areas and oxygen contents of the chromium and nickel powders obtained, their oxygen to surface area ratios varied only from 0.00164 to 0.00317 gram per square meter. This suggests that higher purity powders could be produced by using higher reducing temperatures.

INTRODUCTION

Chromium and chromium base alloys have been receiving increasing attention in recent years as materials with potential for jet-engine and other high-temperature applications. The discussion of the pros and cons of chromium and chromium base alloys for these applications is given in the literature (ref. 1). It is generally considered possible to raise the present level of mechanical properties of chromium to the values required in contemplated high-temperature applications by alloying and/or by dispersion strengthening (ref. 1).

Dispersion strengthening of chromium and its alloys by powder metallurgy appears to offer good chances of obtaining desired properties. The powder metallurgy approach is versatile and easily scaled up. In essence, this dispersion strengthening method consists of obtaining a well-distributed mixture of very fine metals and dispersoid powders followed by consolidation of the mixture by powder metallurgy techniques (ref. 2). If a mechanical blending method is to be used to achieve this fine distribution, ultrafine metal and dispersoid powders are essential (ref. 3). Although some ultrafine dispersoids such as thorium oxide (ThO_2) and aluminum oxide (Al_2O_3) are commercially available, submicron chromium or chromium alloy powders are not. Because of the unavailability of fine chromium and chromium alloy powders, a number of research programs for their production have been undertaken at the NASA Lewis Research Center. The main objective of the present investigation was to produce ultrafine, high-purity chromium powders by reduction of chromic oxide (Cr_2O_3) with volatile reactive metals.

The production of chromium powders has been tried by many diverse methods. One of these methods involves the reduction of Cr_2O_3 with metal vapors. The reduction of Cr_2O_3 with magnesium to produce chromium was first investigated by Kroll, Hergert, and Carmody (ref. 4) and later by Hivert (ref. 5). Hivert modified the method of reference 4 so as to be able to obtain better control of the particle size of the resulting powders. Hivert's modification consists, essentially, in passing magnesium vapor through a bed of Cr_2O_3 with the reactants being maintained at constant temperature in a hydrogen atmosphere. The particle size of the chromium powder is determined by the temperature at which the reaction is allowed to proceed. Hivert claims to have obtained chromium powder down to 0.1-micrometer particle size by this method. However, chromium powders produced by Hivert's method are commercially available only in the micron size range. These powders contain varying amounts of residual magnesium oxide.

The writer thought it possible to obtain still finer particle size chromium and a faster rate of powder production by modifications of the Kroll-Hivert magnesiothermic method for reduction of Cr_2O_3 . These modifications consisted in carrying out the reduction in a vacuum furnace (instead of hydrogen) and in making some design changes in the

reaction vessel. In addition, it was surmised that, because of the tendency of magnesium oxide to form the magnesium oxide - chromic oxide ($\text{MgO} \cdot \text{Cr}_2\text{O}_3$) spinel, reduction of Cr_2O_3 with metal whose oxides are not spinel formers might produce chromium powders with lower oxide content. Thermodynamic considerations such as free energies, vapor pressures, and solubilities led to the choice of lithium and sodium as suitable reducing agents for Cr_2O_3 .

It is believed that, in addition to being capable of producing fine chromium powders suitable for conventional mixing methods of dispersion strengthening, reduction of Cr_2O_3 with magnesium, lithium, and sodium may offer other advantages:

(1) Alloys made from chromium powders produced by reduction of Cr_2O_3 with magnesium (refs. 4 and 5) may have ductility similar to that of chromium-spinel composition (Chrome-30, refs. 6 and 7). In Chrome-30 the magnesium oxide was added intentionally, whereas the magnesium oxide in the chromium powders produced by reduction of Cr_2O_3 with magnesium is formed during processing.

(2) The final processing stages in the production of chromium by the reduction of Cr_2O_3 with metals involves leaching and washing of the chromium powders with water. This production method offers a convenient means of obtaining a dispersion by mixing aquasol type dispersoids such as ThO_2 with the metal powder in suspension (ref. 8).

Experiments were conducted involving the reduction of Cr_2O_3 with magnesium, lithium, and sodium. Reduction of Cr_2O_3 with lithium was carried out at three different temperatures. For comparison purposes, and because nickel is an alloying element in nickel-chromium alloys, nickel powder was produced by reduction of nickel monoxide (NiO) with lithium.

The surface areas and the oxygen content of all the chromium and nickel powders produced were determined. Trace elements (such as nitrogen, carbon, and sulfur) and residual reducing metal present were also determined in some of the powders by chemical analyses.

PROCEDURES

Materials and Equipment

The materials used in this investigation (shown in table I) were reagent-grade chromium oxide (Cr_2O_3), reagent-grade nickel oxide (NiO), high-purity magnesium, high-purity lithium, and high-purity sodium. The chemical analyses or purity of these materials are also shown in table I. Deaerated distilled water, deaerated tap water, and reagent-grade, dilute (approximately 10 N) nitric acid were also used. Both the distilled and the tap water were deaerated at room temperature in a gas tight vessel by applying vacuum until the water boiled.

TABLE I. - CHARACTERIZATION OF RAW MATERIALS

Material (a)	Form or size	Grade	Purity	Manufacturers' specifications (unless otherwise noted)		
				Impurity	Content	
					ppm	wt %
Chromic oxide (Cr ₂ O ₃)	Powder, ^b 0.66 μm	High purity	(c)	Nitrogen (N)	412	----
				Sulfur (S)	334	----
				Chlorine (Cl)	30	----
				Iron (Fe)	300	----
				Substances not precipitated by ammonium hydroxide	-----	0.5
Nickel monoxide (NiO)	Powder, ^b 0.95 μm	High purity	(c)	Nitrogen (N)	50	----
				Sulfur (S)	^d 33	----
				Chlorine (Cl)	50	----
				Heavy metals (lead, copper, etc.,)	-----	0.26
				Alkaline and earth metals (as sulfate (SO ₄))	-----	.20
Magnesium (Mg)	Bars (38 mm in diam)	Prime grade	99.8 minimum	(c)	-----	----
Lithium (Li)	Sticks (12.5mm in diam)	High purity	99.5 minimum	Nitrogen (N)	^d 348	----
				Carbon (C)	^d 344	----
				Sulfur (S)	Not detected, ^d <100	----
Sodium (Na)	Ingots (approximately 450 g each)	High purity	(c)	Nitrogen (N)	30	----
				Chloride (Cl)	20	----
				Phosphate (PO ₄)	5	----
				Sulfate (SO ₄)	Past test	----
				Heavy metals (lead, etc.,)	5	----
				Iron (Fe)	10	----

^aNames of suppliers will be given to qualified requesters.^bParticle sizes were obtained with the Fisher subsieve sizer.^cNot determined or unknown.^dFrom chemical analyses.

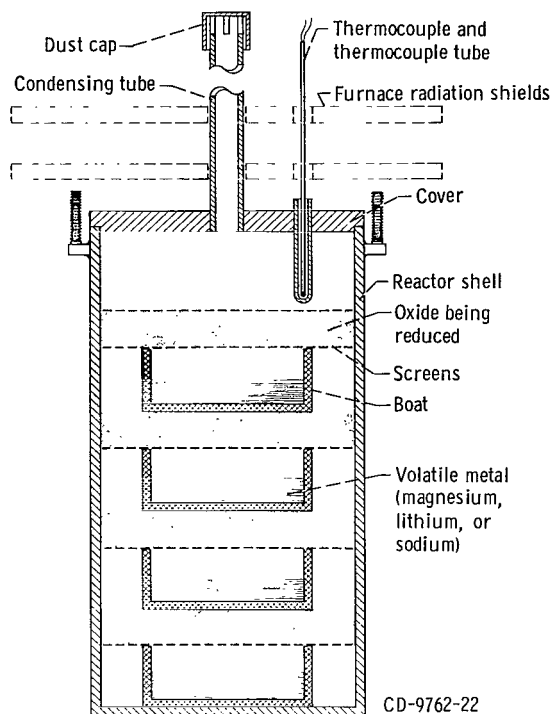


Figure 1. - Reactor in furnace.

The main pieces of equipment used in this investigation were a reaction vessel (shown in fig. 1), a furnace, and a centrifuge.

Process Flow Charts

Figure 2 is the process flow chart for the reduction of Cr_2O_3 with magnesium, and figure 3 is the process flow chart for the reduction of Cr_2O_3 with either lithium or sodium and for the reduction of NiO with lithium. The temperatures and times used to reduce the oxides in the various experiments are shown in table II. The details about equipment and procedures used for the various steps in the flow charts follow.

Loading Reactor

Loading the reactor was the first step in the reduction process. The reactor is the vessel in which the reactants (oxides and reactive metals) were heated to the temperature at which reaction was to take place. The entire reactor was heated in a vacuum furnace (described in the following section). A sketch of the type of reactor used is shown in

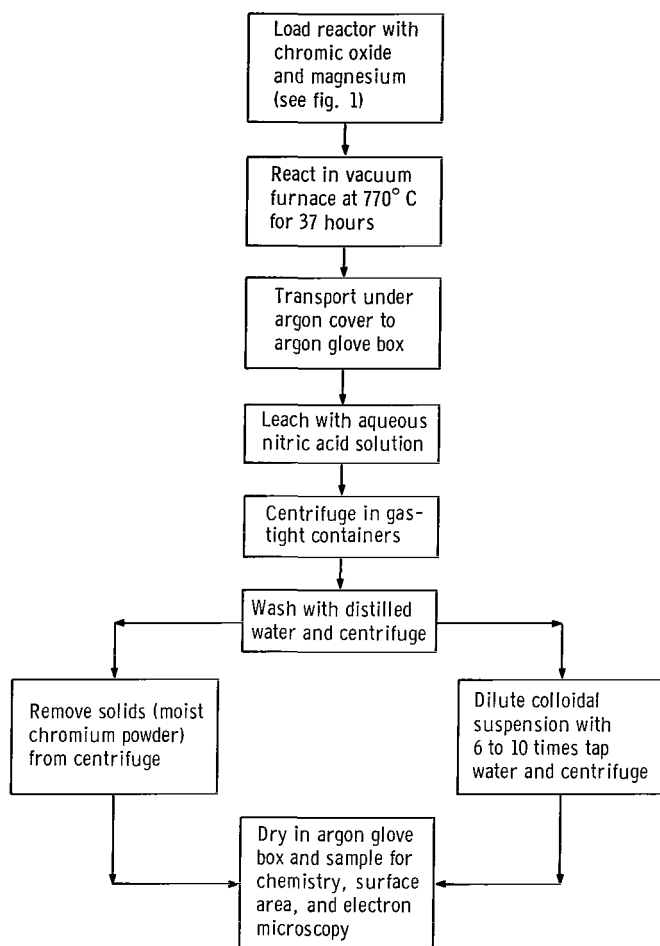


Figure 2. - Flow chart for reduction of chromic oxide with magnesium vapor.

figure 1. All the parts of the reactor were made from stainless steel. In the figure, the reactor is shown with the cover used during reaction in the furnace. If required, the reactor could be closed with a gas-tight lid during transportation and loading into the furnace.

About 20 to 400 grams of oxide were reacted at a time in the reactors. The amounts of reactants to be used in a run were determined by preliminary trial runs. About twice the amount of reactive metal required for stoichiometric reduction of the oxide was used in each run, so that at the end of the run some reactive metal would remain unreacted. This ensured that any residual oxygen in the vacuum furnace atmosphere would react with the reactive metal vapor and not with the powdered metal being made. These operating conditions meant that, in most cases, the reactive metal vapor went through the top oxide layer (see. fig. 1) and condensed in the tube attached to the cover.

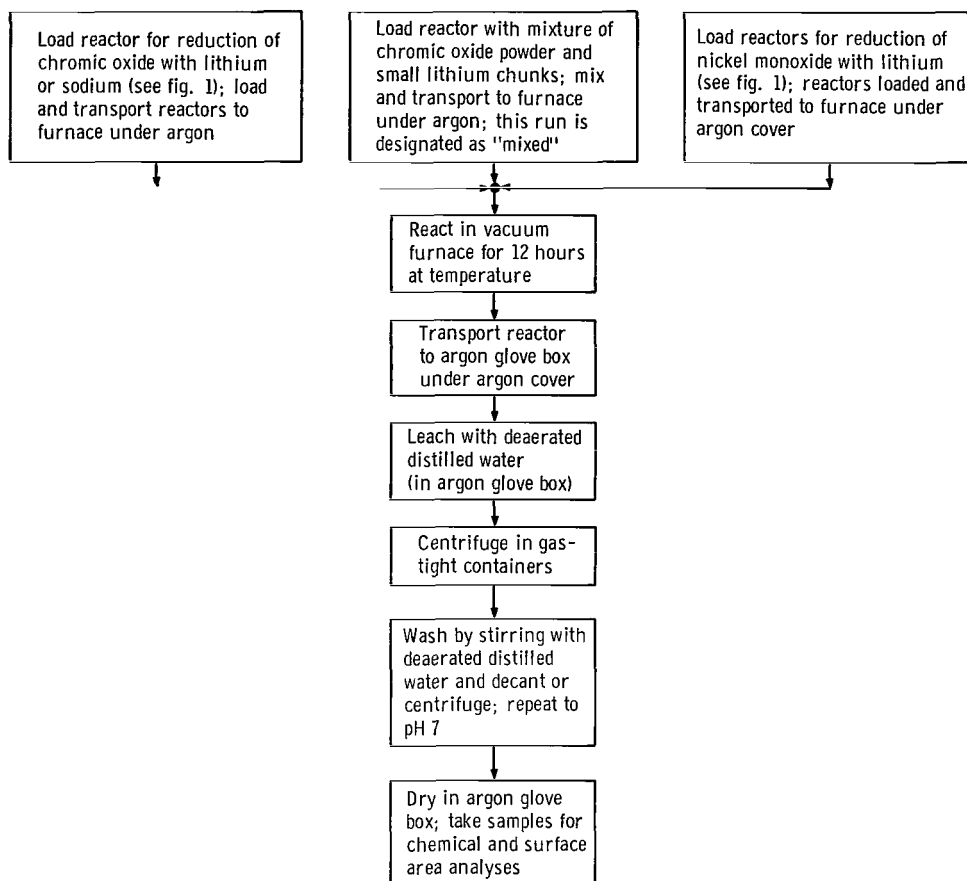


Figure 3. - Flow chart for reduction of chromic oxide with lithium or sodium vapors and for reduction of nickel monoxide with lithium vapor.

The alternating stacked arrangement of the reactive metal and oxide (shown in fig. 1) allows fast production rates, first, because reaction can occur simultaneously in all the oxide beds and, second, because in the intermediate oxide beds the oxide is attacked by the metal vapor from above and from below the bed.

In one of the runs with Cr_2O_3 and lithium, because of the low temperature used, even the stacked arrangement described proved to be too inefficient in powder production. In order to increase the powder production rate for this run, the Cr_2O_3 was mixed by hand with pea size lithium chunks and loaded into the same reactor, but without the screens and boats. However, this procedure could be used only at the lower temperatures because at the higher temperatures, the highly exothermic reaction could not be controlled. To distinguish this type of loading from the normal type of loading, this particular run will be designated as "mixed." This method was also tried for the reduction of NiO with lithium.

TABLE II. - REACTING CONDITIONS FOR REDUCTION OF CHROMIC OXIDE WITH MAGNESIUM, LITHIUM, AND SODIUM
AND OF NICKEL MONOXIDE WITH LITHIUM; CHEMICAL ANALYSIS, SURFACE AREA, PARTICLE SIZE, AND
OXYGEN TO SURFACE AREA RATIO OF RESULTING CHROMIUM AND NICKEL POWDERS

Oxide - reducing-metal system	Loading of reactants	Reacting conditions		Chemical analysis of resulting metal powders				Specific surface area, S, m ² /g	Particle size, ^a μm	Oxygen to surface area ratio, O/S, g/m ²	Remarks
		Temperature, °C	Time, hr	Oxygen, percent	Nitrogen, ppm	Carbon, ppm	Other, percent				
Chromic oxide - magnesium (Cr ₂ O ₃ -Mg)	See fig. 1	770	37	1.74	90	477	Magnesium (Mg), 1.16	3.47	0.16	0.0050	Coarse chromium fraction (fig. 2)
				2.24	864	(b)	(b)	80.9	0.00685	0.00028	Colloidal chromium fraction (fig. 2)
				1.76	129	(b)	(b)	7.35	0.075	0.0025	Calculated "bulk" values ^c
Chromic oxide - lithium (Cr ₂ O ₃ -Li)	Mixed	420	12	1.50	79	1500	Sulfur (S), 0.050	7.14	0.078	0.0021	
	See fig. 1	600	12	0.678	(b)	(b)	Lithium (Li), 0.007	4.14	0.134	0.0016	
		800	12	0.176	(b)	(b)	Lithium (Li), 0.015	0.93	0.598	0.0019	
Chromic oxide - sodium (Cr ₂ O ₃ -Na)	See fig. 1	510	12	7.14	(b)	(b)	Sodium (Na), 2.14	37.0	0.015	0.0019	
Nickel monoxide - lithium (NiO-Li)	See fig. 1	600	12	0.114	(b)	(b)	Lithium (Li), 0.080	0.36	1.25	0.0032	

^aCalculated from equation (developed in ref. 3): Particle size (μm) = 4/ρS, where ρ is density (g/cm³) and S is surface area (m²/g).

^bNot determined.

^cCalculated "bulk" values are weighted averages of the coarse chromium fraction (95 weight percent) and colloidal chromium fraction (5 weight percent). See text for more details.

For the run of Cr_2O_3 with magnesium, the reactor was loaded in air. For all other runs, the reactor was loaded in an argon glove box and transported under argon to the furnace.

Reacting in Vacuum Furnace

The reactor was heated to the required reaction temperature in an induction-heated, top-loading, vacuum furnace. This furnace has a graphite susceptor and carbon black insulation. During loading or unloading of the reactor, this furnace could be flooded with argon while the gas-tight lid was being removed from or screwed on the reactor. For all reaction runs, except that with Cr_2O_3 and magnesium, the reactors were placed in the furnace under argon.

After loading the reactor into the furnace and covering it with the type of vented cover shown in figure 1, the furnace was evacuated to a pressure of less than 0.1 micrometer of mercury (0.013 N/m^2) and heated to the required temperature. At no time during the runs reported in table II did the temperatures vary by more than $\pm 10^\circ \text{C}$, nor did the pressure exceed 5 micrometers of mercury (0.67 N/m^2). The 12-hour runs (fig. 3 and table II) were made in a continuous heating period; the 37-hour run (for the reduction of Cr_2O_3 with magnesium) was made in several heating periods. At the end of each run, the cool furnace was again flooded with argon, the gas-tight lid screwed on the reactor, and the reactor taken to an argon glove box for further processing of the reaction products. The operations described hereinafter, unless noted otherwise, were performed in an argon glove box filled with high-purity argon.

Leaching and Washing

The reaction products were mixtures of the metal being produced (either chromium or nickel) and the oxide of the reactive metal (i. e., magnesium oxide (MgO), lithium oxide (Li_2O), or sodium oxide (Na_2O)). The magnesium oxide produced by the reaction of Cr_2O_3 with magnesium was separated from the chromium - magnesium oxide mixture by leaching with nitric acid (in which chromium is insoluble). Lithium oxide and sodium oxide were removed from their mixtures with the metal being produced by leaching these oxides with pure water.

The friable, powdery mixture of chromium metal powder and magnesium oxide obtained by magnesiothermic reduction of Cr_2O_3 was leached with dilute nitric acid added dropwise with constant stirring. The amount of acid used was in excess of that required to leach the magnesium oxide as calculated from the weight of the recovered reaction

products. The nitric acid - powder mixture was digested for about 14 hours before separating the liquid from the metal by centrifuging in gas-tight containers (or centrifuge buckets). The pH of the final solution was well below 1. The centrifuging was carried out outside the argon glove box, but the centrifuge buckets were loaded and unloaded inside the box. The powder residue was washed several times with deaerated distilled water by stirring the powder-water slurry, followed by separation by centrifuging in gas-tight containers while monitoring the washing of the powder with pH paper strips. On reaching a pH of about 4.5, a finer fraction of the chromium powder became suspended as a colloid in the wash water, while a coarse fraction of the powder sank to the bottom of the centrifuging container. The coarse fraction of the powder was washed several times until a wash water (colloidal suspension) with pH near 7 was obtained. The coarse fraction of the chromium powder in the bottom of the centrifuging containers was recovered for further processing. All the washings with the colloidal chromium in suspension were diluted with 6 to 10 times their own volume of deaerated tap water and centrifuged in gas-tight containers. Tap water was used only on the colloidal fraction obtained because it was effective to precipitate the colloid. The colloidal chromium powder was washed several times with deaerated tap water to pH near 7 and again separated from the wash water by centrifuging. Complete recovery of the colloidal chromium (in the original distilled water washings) was obtained in this manner.

The chromium and nickel powders, obtained by reduction of the corresponding oxides with lithium, were leached and washed with deaerated distilled water until the washings showed a pH near 7 (as measured with pH paper strips). The powders were separated from the water by decantation. The chromium powder obtained by reduction of Cr_2O_3 with sodium was leached and washed with deaerated distilled water until the wash water showed a pH of about 7. The chromium was separated from the water by centrifuging. No colloidal suspensions were observed in the wash water of the powders obtained by lithium or sodium reduction perhaps because the pH was above 7.

Drying

The moist powders obtained either by decantation or by centrifuging were first dried at room temperature by evacuation in the argon glove box down to a pressure of about 1 micrometer of mercury (0.13 N/m^2). The powders were further dried by heating to about 150°C also to about 1 micrometer of mercury (0.13 N/m^2) under vacuum.

Analyses of Powders

Samples of each of the dry powders were loaded in the argon glove box into tin capsules for oxygen analyses. The surface areas of all the powders obtained were determined by the BET method (ref. 9). Some of the powders were analyzed for elements other than oxygen and/or residual reactive metal. Electron photomicrographs of the "colloidal" chromium obtained by magnesium reduction of Cr_2O_3 were taken.

RESULTS

Preliminary Runs

Preliminary experiments for the reduction of Cr_2O_3 with magnesium were conducted under various conditions. For example, on reducing Cr_2O_3 with magnesium in a vacuum furnace and at temperatures up to about 800°C , the resulting chromium - magnesium oxide mixtures were black and powdery. At about 800°C , the reaction through the Cr_2O_3 layer proceeded at a rate of about 3 millimeters per hour (in the top layer). On heating a reactor, loaded as shown in figure 1, to about 850°C , the reactor temperature suddenly increased to about 1200°C , indicating that a self-sustaining reaction had been started. The resulting chromium - magnesium oxide mixture was light gray and friable. After leaching, the resulting chromium powder was quite coarse with individual powder particles being visible without magnification.

Preliminary runs conducted at about 750°C for the reduction of Cr_2O_3 with sodium showed that only a very thin layer of Cr_2O_3 just above or below each of the sodium containers had reacted with the sodium vapor. The reason for this was that most of the remainder of the Cr_2O_3 layer had become impervious and almost as hard as cement. In fact, the sodium boats had to be removed by drilling the Cr_2O_3 layers with a tungsten carbide tipped trepaning tool. During a run at 900°C , the sodium vapor channeled through the Cr_2O_3 layer and condensed in the cool portion of the condensing tube.

Similar preliminary experiments were conducted for the reduction of Cr_2O_3 and NiO with lithium. On the basis of all these preliminary experiments, the reducing temperatures were chosen so that sufficient amounts of chromium or nickel powders for chemical and BET analyses were obtained in a reasonable time.

Reduction of Chromic Oxide with Magnesium

The results of surface area and chemical analyses of both the colloidal and the rel-

atively coarse fractions of the chromium powder obtained by magnesiothermic reduction of Cr_2O_3 at 770°C are shown in table II. It should be noted that the colloidal chromium fraction is extremely fine ($0.0068\ \mu\text{m}$) compared with the coarse chromium fraction ($0.16\ \mu\text{m}$). Considering the large surface area of the colloidal powder, its oxygen content (2.24 weight percent) is quite low and only about 1.3 times that of the coarse fraction. Its nitrogen content (864 ppm), though much lower than the oxygen content, is about 10 times that of the coarse fraction of the powder. The chromium obtained by magnesium reduction was the only powder that was separated into two fractions (5 weight percent colloidal and 95 weight percent coarse). The results for these two powder fractions are given in table II. The weighted average of the results for the two fractions (which is equivalent to the unseparated powder) will be used for comparison with the powders obtained by reduction of Cr_2O_3 and NiO with lithium and sodium. The weighted average will be termed the "calculated bulk value" under consideration. Thus, the calculated bulk surface area of the chromium obtained by magnesium reduction is

$$0.95 \times 3.47 \frac{\text{m}^2}{\text{g}} + 0.05 \times 80.9 \frac{\text{m}^2}{\text{g}} = 7.35 \frac{\text{m}^2}{\text{g}}$$

This value and other calculated bulk values for the chromium obtained by magnesiothermic reduction of Cr_2O_3 are included in table II.

Figure 4 is an electron photomicrograph of the colloidal fraction of the chromium powder. It is noteworthy that this powder has fairly uniform and equiaxed particles and a tendency to form large agglomerates.

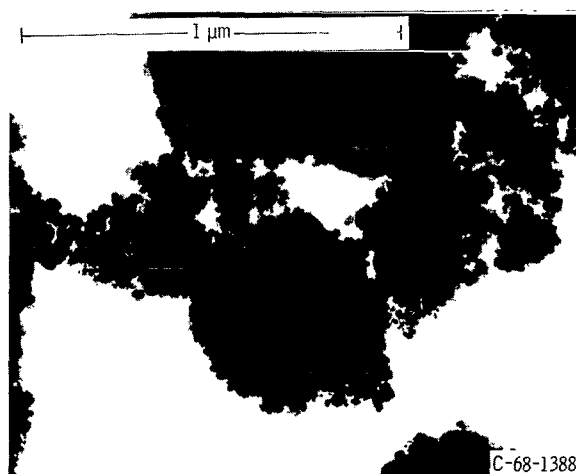


Figure 4. - Electron photomicrograph of colloidal fraction of chromium powder obtained by magnesiothermic reduction of chromic oxide.

Reduction of Chromic Oxide with Lithium

In the 420° to 800° C temperature range covered in this investigation (table II), the mixtures of chromium and Li_2O resulting from the reaction of Cr_2O_3 with lithium were black and crumbly. At about 800° C, the reaction rate of lithium with Cr_2O_3 was much slower than that of magnesium with Cr_2O_3 . During leaching and washing, the chromium powders settled readily with no tendency to form colloidal suspensions.

Both the surface areas of the powders and the oxygen contents decrease with increasing reduction temperature (table II). The chromium powder obtained by reduction with lithium at 800° C has a much smaller surface area (much larger particle size) and lower oxygen content than the bulk of the chromium obtained by magnesium reduction at 770° C - despite the much longer time at temperature (37 hr compared with 12 hr) for the latter. It should also be noted that the residual lithium retained is nearly 1/80 of the residual magnesium retained at equivalent temperatures.

Reduction of Chromic Oxide with Sodium

During the run at 510° C for the reduction of Cr_2O_3 with sodium reported in table II, a usable brown colored mixture of chromium powder and Na_2O was obtained. The particle size of this chromium powder is 0.015 micrometer; the content of oxygen is 7.14 weight percent; and the residual sodium is 2.14 weight percent.

Reduction of Nickel Monoxide with Lithium

The reaction of NiO with lithium at 600° C yielded a dark gray powder. The nickel powder could be separated rapidly after leaching and washing by decantation. This powder is fairly coarse (1.25 μm) and low in oxygen (0.114 weight percent) and residual lithium (0.08 weight percent).

Attempts were made to obtain finer nickel powders by reacting mixtures of NiO with lithium chunks (similar to the Cr_2O_3 - lithium mixture reacted at 420° C) at temperatures below 600° C. However, these NiO - lithium chunk mixtures showed a tendency to react spontaneously even at room temperature during mixing. For this reason, the attempt to obtain finer nickel powders was abandoned.

DISCUSSION OF RESULTS

The results obtained by reactive metal vapor reduction have demonstrated the feasibility of producing very fine and moderately pure chromium and nickel powders from their oxides. Reduction of Cr_2O_3 with magnesium, lithium, and sodium vapors produced chromium powders ranging in size from 0.007 to 0.6 micrometer and oxygen contents ranging from 0.176 to 7.14 weight percent. Reduction of NiO with lithium produced a nickel powder with an average particle size of 1.25 micrometer and 0.114 weight percent oxygen.

Particle Sizes

The reduction of Cr_2O_3 with magnesium yielded chromium powder with two fractions of widely different average particle sizes. The coarse fraction of the powder (about 95 weight percent of the total) which remained in the buckets after washing and centrifuging with distilled water had an average particle size of 0.16 micrometer. This particle size is fine enough for dispersion strengthening purposes. The fine (or colloidal) fraction of the powder (representing about 5 weight percent of the total) had an average particle size of 0.0068 micrometer. Even though the yield of this fine powder was small, this process could be scaled up to yield significant quantities of the finest chromium powder ever reported in the literature. This process may also work for the separation of other fine metal powders into fractions.

The calculated bulk particle size ($0.075 \mu\text{m}$) of the chromium powder obtained by magnesiothermic reduction of Cr_2O_3 compares favorably with the 0.1-micrometer chromium powder obtained by Hivert (ref. 5).

The series of chromium powders obtained by lithium reduction of Cr_2O_3 showed that the lower the reduction temperature, the smaller the particle size of the powder (and the higher the oxygen content). The increase in particle size with increasing temperature was to be expected in view of the increase in growth rate of powder particles with temperature observed in connection with sintering.

The particle size of the chromium obtained by lithium reduction of Cr_2O_3 at 800°C is 0.598 micrometer as compared with a calculated bulk particle size of 0.075 micrometer for the chromium obtained by magnesium reduction of Cr_2O_3 at 770°C . Quite obviously and despite the differences in reacting temperature and time at temperature, magnesium reduction of Cr_2O_3 is capable of producing much finer chromium powder than lithium reduction of Cr_2O_3 .

The chromium powder produced by the reduction of Cr_2O_3 with sodium at 510°C was 0.015 micrometer in average particle size. By comparison, the chromium powders

obtained by lithium reduction at 420° and 600° C were 0.078 and 0.134 micrometer average particle size, respectively. On the assumption that the particle sizes of the chromium obtained by magnesium and sodium reductions of Cr_2O_3 follow the same particle-size - temperature law as for lithium reduction, extrapolation of the magnesium reduction particle size data to lower temperatures shows that sodium is capable of producing finer "bulk" particle size chromium than magnesium reduction. Unfortunately, sodium reduction of Cr_2O_3 is of limited applicability because, as shown later, in order to obtain powders with lower oxygen content, the particle size must be increased by increasing the reaction temperature. But, as indicated under RESULTS, at high temperatures the unreacted Cr_2O_3 hardens and becomes impervious to the passage of sodium vapor.

The nickel produced by reduction of NiO with lithium at 600° C was 1.25 micrometer average particle size. Although coarse, this nickel powder is comparable in particle size with commercially available nickel powders prepared by other methods.

It should be noted that the particle size of the nickel powder produced by reduction of NiO with lithium is about 10 times larger than that of the chromium powder produced under identical conditions (see table II). At least in part, this larger nickel particle size must be a result of the greater sinterability of nickel. In order to obtain fine nickel powder, very low reaction temperatures must be used, and this may render the process both slow and expensive.

Powder Purity

Oxygen and residual reducing metal. - The metal powders prepared by various methods in this investigation varied in oxygen content from 0.114 to 7.14 weight percent (table II). The powder with the lowest oxygen content (0.114 weight percent) was the nickel obtained by reduction of NiO with lithium. This powder has a lower oxygen content than some commercially available nickel powders of still larger particle size. For this reason it may be suitable for comminution to smaller particle sizes by grinding.

The chromium powders with the lowest oxygen contents were those obtained by reduction of Cr_2O_3 with lithium. Residual reducing metal in the product was also least with lithium. The lithium content in three chromium powders ranged from 0.007 to 0.08 weight percent. These residual lithium contents were 0.1 to 0.01 of the residual content of either sodium or magnesium in the other powders.

The "bulk" chromium powder obtained by reduction of Cr_2O_3 with magnesium has a higher oxygen content than that obtained by lithium reduction at equivalent temperatures. The residual magnesium in these powders is also high when compared with the residual lithium. Although the relatively high oxygen and magnesium may be high from the purity point of view, these impurities may be an advantage when the powders are considered

for dispersion strengthening purposes. The reason for this is that the magnesium quite probably is in the form of (or will eventually become after high-temperature sintering) MgO, and this MgO either alone or as the spinel $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ may act as a dispersion strengthener. This dispersion strengthening by MgO is discussed in more detail later.

The chromium powder with the highest oxygen content (7.14 weight percent) was that obtained by reduction of Cr_2O_3 with sodium. Possibly, this high oxygen content is caused in part by the small particle size of this powder and by the tendency of Na_2O to form glasses with oxides of other metals.

Other impurities. - Spots checks of carbon, nitrogen, and sulfur were conducted. The impurities (C, N, and S) shown in table II probably originate in the raw materials or were picked up (particularly carbon) from the furnace atmosphere.

The results of this investigation show that, in general, it is possible to produce fine and moderately pure chromium and nickel powders by the reduction of the respective oxides with reactive, volatile metal vapors. It appears that even higher purity powders could be obtained by using raw materials of higher purity, and a very-high-vacuum, carbon-free furnace.

Oxygen to Surface Area Ratio

Another manner in which metal powders can be compared is by consideration of the oxygen to surface area ratio O/S. These ratios (in grams of oxygen per square meter of powder surface) for the powders produced in this investigation are included in table II.

The surface areas of all the "bulk" chromium powders produced by different methods ranged from 37 to 0.93 square meter per gram, that is, by a factor of about 40. The oxygen contents of the chromium powders ranged from 7.14 to 0.176 weight percent, that is, also by a factor of about 40. Yet, the O/S ratio for the entire group of powders varied only from 0.0025 to 0.00164 or by a factor of only 1.53. The obvious indication of this result is that most of the oxygen content of the powders must be on the surface of the powder particles, perhaps as a result of reaction with the wash water.

From the point of view of the O/S ratio, there appears to be little difference between the powders produced by magnesium, lithium, or sodium as reducing agents. Also, reducing temperatures (as shown by the ratios for lithium reduced powders) appear to have little effect on this ratio. In fact, assuming this constancy of O/S ratio to higher temperatures, larger particles of similarly reduced material would have very low oxide contents. For example, a chromium powder about 12 micrometers in size obtained by lithium reduction of Cr_2O_3 would have an oxygen content of about 100 ppm.

It should be noted that the colloidal fraction of the chromium obtained by magnesio-thermic reduction of Cr_2O_3 has the lowest O/S ratio (0.00028 g/m^2). This low ratio is

attributed to sorption of (unknown) ions from either the tap water or nitric acid in the wash water in which this fraction was separated. A coating of adsorbed or chemisorbed ions (other than oxygen) might conceivably protect the powder from (oxidation by) reaction with water.

It is seen in table II that the highest O/S ratio for "bulk" powders is that for nickel. Although still not larger than twice the lowest ratio obtained for chromium, this relatively high value for nickel may be an intrinsic property of the nickel system.

Suitability of Powders Produced for Dispersion Strengthening

Superior quality dispersion strengthened products require small interparticle spacings and hence small particle size starting powders (ref. 3). On the other hand, the higher the oxygen content of the metal powder, probably the greater the structural instability of the oxide dispersoids (ref. 10). Hence, considering both particle size and purity, the suitability of the powders obtained in this investigation for dispersion strengthening purposes is probably just as good (particularly those obtained by lithium reduction) as some commercially available chromium and nickel powders used for ball milling with dispersoids. As indicated in the previous discussion on the O/S ratio, oxygen contents even lower than those of the purest commercially available chromium and nickel powders are possible. An added advantage of lithium reduction is that alloys of nickel and chromium in any proportions can quite probably be obtained by reduction of the corresponding NiO-Cr₂O₃ composition. This oxide composition could quite conceivably be obtained by melting or by plasma spraying of a mixture of the two oxides. Further, since ThO₂ is not reduced by lithium (ref. 11), the reduction of NiO-Cr₂O₃-ThO₂ alloy by lithium vapors could lead to nickel-chromium alloys with a "built in" dispersoid (ThO₂). Although these metal dispersoid systems are hypothetical, the reduction techniques developed in this investigation indicate that the production of chromium - MgO or chromium - MgO · Cr₂O₃ alloys is quite feasible.

As shown in table II, the coarse fraction of the chromium obtained by magnesium reduction of Cr₂O₃ contains 1.74 weight percent oxygen and 1.16 weight percent magnesium. The residual magnesium may be assumed to be present as MgO and the excess oxygen tied up as Cr₂O₃. A simple calculation shows that 100 grams of the coarse fraction of the chromium powder could contain $(40.32/24.32) \times 1.16 = 1.92$ grams of MgO. Since 1.92 grams of MgO contain 0.761 gram of oxygen, the remainder of the oxygen $(1.74 - 0.761) = 0.979$ gram must be tied up as $(152.02/48) \times 0.979 = 3.10$ grams of Cr₂O₃. These 3.10 grams of Cr₂O₃ can combine with $(40.32/152.02) \times 3.10 = 0.822$ gram of MgO to form $(3.10 + 0.822) = 3.922$ grams of MgO · Cr₂O₃ spinel. Hence, the alloy could have 3.92 weight percent of MgO · Cr₂O₃ spinel plus $(1.92 - 0.822) = 1.098$

weight percent MgO. This is equivalent to 2.16 volume percent MgO plus 5.52 volume percent spinel for a total of 7.68 volume percent dispersoids. This volume percent dispersoid is considered quite suitable for dispersion strengthening. Of far greater significance in this particular system, however, is the fact that MgO and the $\text{MgO} \cdot \text{Cr}_2\text{O}_3$ spinel are known to ductilize chromium (refs. 6 and 7). Thus, the chromium obtained by magnesium reduction of Cr_2O_3 is not only of a particle size suitable for dispersion strengthening, but it also has suitable amounts of dispersoids, and the consolidated product may be ductile at room temperature. Whether this product would meet stability and strength requirements is another matter beyond the scope of the present investigation.

SUMMARY OF RESULTS AND CONCLUSIONS

The results and conclusions of the present investigation, conducted for the purpose of producing high purity chromium and nickel powders suitable for dispersion strengthening, are as follows:

1. The chromium powder obtained by reduction of chromic oxide (Cr_2O_3) with magnesium vapor at 770°C was separable into a colloidal and a coarse fraction. The colloidal and coarse fractions had average particle sizes of 0.00685 and 0.16 micrometer, respectively. The 0.00685-micrometer colloidal fraction of the powder is the smallest particle size chromium powder reported in the literature.

2. Reacting conditions being equivalent, the ability of lithium, magnesium, and sodium to produce fine particle size chromium increases in that order (as surmised from extrapolation of data). Reduction of Cr_2O_3 with sodium, however, is of limited applicability because unreduced Cr_2O_3 hardens and becomes impervious to the passage of sodium vapors because of reaction between volatile sodium oxide (Na_2O) and Cr_2O_3 .

3. Although the nickel powder obtained by reduction of nickel monoxide (NiO) with lithium at 600°C is rather coarse ($1.25\ \mu\text{m}$) it has low oxygen content (0.114 weight percent). The particle size is comparable to and the purity of this powder is higher than that of some commercially available nickel powders presently used for dispersion strengthening. Production of very fine nickel powder by this method is hindered by very slow reaction rates, because production of very fine powders requires very low reaction temperatures.

4. The chromium powders produced by reaction of Cr_2O_3 with lithium have lower oxygen content and much lower residual reducing metal than the chromium powders obtained by reduction with either magnesium or sodium. The lower oxygen content of chromium powders obtained by lithium reduction may result from the larger particle sizes of these powders.

5. Although the surface areas of the "bulk" chromium powders obtained varied by a factor of about 40 and the oxygen contents also by a factor of about 40, the ratio of oxygen content to surface area (O/S) varied by a factor of less than 2. This indicates that most of the oxygen is on the surface of the powders and that this oxygen probably resulted from the reaction of the metal with water.

The O/S ratio is fairly insensitive to reaction temperature. The constancy of this ratio indicates that coarse chromium powders with low oxygen content (e. g. , 12- μ m chromium with 100 ppm oxygen) or fine chromium powders with high oxygen content should be obtainable by conducting the reaction at higher or lower temperatures, respectively.

6. Some of the chromium powders obtained had from 79 to 864 ppm of nitrogen, 477 to 1500 ppm of carbon, and about 500 ppm of sulfur. Much higher purity chromium should be obtainable by using purer raw materials and a carbon-free, vacuum furnace.

7. Since both chromium and nickel powders were obtained by reduction of the corresponding oxides, it should be possible to obtain nickel-chromium (and perhaps nickel - chromium plus dispersoid) alloy powders by lithium reduction of the pulverized melt of the corresponding oxides.

8. The coarse fraction of the chromium powder obtained by reduction of Cr_2O_3 with magnesium vapor at 770°C have particle sizes and amounts of dispersoids ($\text{MgO} + \text{MgO} \cdot \text{Cr}_2\text{O}_3$) suitable for dispersion strengthening without further processing except consolidation. These results suggest that, if consolidated, this chromium alloy could have a low ductile-to-brittle transition temperature.

Lewis Research Center,
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